O-343

ISOLATION AND CHARACTERIZATION OF BARIUM SULPHATE AND TITANIUM OXIDES IN MONUMENTS CRUSTS

J.L. PÉREZ-RODRÍGUEZ[1], M.C. JIMÉNEZ DE HARO[1], C. MAQUEDA[2]

[1]Instituto de Ciencia de Materiales de Sevilla, CSIC-UNSE, 41092 Sevilla, Spain

[2]Instituto de Recursos Naturales y Agrobiología. P.O. Box 1052, 41080 Sevilla, Spain

The surface layers of ornamental materials of monuments and historic buildings are altered by the interaction of the original materials with environmental pollutants, producing weathering crusts on the exposed surface. Different studies have shown that the surface layers of ornamental materials may contain many components from the environment and/or from the alteration processes. Although there are many works on the elements present in polluted surface layers, little attention has been given to the presence of titanium and barium, particularly the latter. Both elements are present in rock materials of historic buildings; in addition, barite may be added to the surface of ornamental materials for consolidation. Ti and Ba containing materials, are present in crusts. They are in low proportion, making them (and particularly the latter) difficult to characterise by mineralogical techniques, such as X-ray diffraction. For this reason, works on the mineralogical composition of the two elements in monument crusts are scarce. Therefore, for a better understanding of the alteration processes of ornamental material, it is important to determine Ba and Ti in the surface layers, and the phases in which they are present, especially when they are in low concentration. The aim of this study is to present an experimental method for the isolation and characterisation of barium sulphate and titanium oxides in the surface layers on ornamental monuments.

Isolation Method. Crust samples from Sevilla Cathedral were taken and an isolation method for barium and titanium components used. After removal of the water-soluble anions, the samples were dried and digested with an acid mixture (HNO_3, HCl, $HClO_4$). The residue was digested with dilute HCl, separated by centrifugation, washed several times with distilled water, and dried at 60°C.

Characterization of the isolated material. The crystalline phases of the residue were characterised by X-ray diffraction (XRD) using a Siemens diffractometer, model kristalloflex D-501, with a graphite monochromator and fixed slits of 1°, 1°, 1° and 0.15°.

Quantitative estimation of the minerals by X-ray diffraction was performed following the method proposed by Chung (1975). Scanning electron microscopy (SEM) was carried out with a Jeol JSM5400 apparatus, equipped with an X-ray dispersive energy analyser (EDAX). Before examination, the samples were made conductive by coating with gold or graphite.

The chemical analysis by EDAX of some particles observed by SEM, shows five-peak patterns characteristic of Ba at 3.95 keV (Le), 4.46 keV ($L\alpha^1$), 4.82 ($L\beta^1$), 5.15 ($L\beta^2$) and 5.53 keV

($L\gamma^1$). The two strongest peaks at 4.46 keV and 4.83 keV overlap the two peaks of titanium, being possible to confirm the presence of barium on the basis of the multipeak patterns. Other particles with different morphology, observed by SEM, show only two peaks at 4.46 keV and 4.83Kev characteristics of titanium.

The X-ray diffraction patterns of the residue shows diffractions at 3.44, 3.10, 2.10 Å, etc. are attributed to barite (barium sulphate), and those at 3.24, 2.46, 1.68 Å, etc., and at 3.52, 2.37, 1.89 Å, etc., are attributed to rutile (titanium oxide) and anatase (titanium oxide) respectively, corresponding with the two different particles observed by SEM.

Quantitative analysis of the elements of the residue can be performed by energy dispersive X-ray microanalysis. The ratio S/Ba of intensities acquired from pure barite may be used to determine the contribution of the barium peak to the overlapped peak of titanium and barium. With this analytical technique, it is possible to determine the chemical composition of, but not the percentages of the three phases present in, the sample. For this reason, the quantitative analysis of the phases present in the residue has been carried out by X-ray diffraction using the Chung method. The intensities of the patterns have been measured to the following planes: anatase: plane (101) $2\theta = 25.3$; barite: plane (210) $2\theta = 25.8$; rutile: plane (110) $2\theta = 27.4$ and compared with the intensity of the plane 220 at $2\theta = 47.05$ of fluorite (CaF_2) used as internal standard.

The percentages of the different components of the residue after heating were estimated in triplicate, with the following results: anatase 8.1%; barite 73.7%; rutile 18.2%.

The method proposed permits the isolation and characterization of barite, anatase, and rutile present in the surface layers of ornamental materials in polluted areas.

REFERENCES

Chung F.H. (1975) *J. Appl. Cryst*:17.